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14. ABSTRACT This report results from a contract tasking Adam Mickiewicz University as follows: High-pressure x-ray diffraction will be applied for investigating the nature of halogen-halogen interactions. These interactions are best observed in substances where no other strong intermolecular forces are present. Such substances are liquids which will be pressure frozen in a diamond-anvil cell, and their crystal structure will be determined by X-rays.					
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Studies of Halogen Bonding Using High-Pressure Diffractometry

ABSTRACT

A series of 1,2-dihalotetrafluoroethanes $X(CF_2)_2Y$ ($X=Br, I$; $Y=Br, I$) – 1,2-dibromotetrafluoroethane ($BrCF_2CF_2Br$), 1,2-diiodotetrafluoroethane (ICF_2CF_2I) and 1-bromo-2-iodotetrafluoroethane ($BrCF_2CF_2I$) – and two other fluorinated compounds (pentafluoropyridine, C_5F_5N ; trifluoromethyl(trimethyl)silane, $CF_3Si(CH_3)_3$), have been in-situ pressure frozen in a diamond-anvil cell and their structures determined by X-ray diffraction. Also complexes of the dihalotetrafluoroethanes with 1,4-dioxane, 1mol:1mol, were investigated using high-pressure X-ray diffraction. The intermolecular interactions in these compounds, and particularly the halogen...halogen, halogen...oxygen and halogen...nitrogen forces have been characterized, and the structure-relation properties studied. The characteristic behavior of the compounds investigated, like a tendency to form strong interactions involving the halogen atoms, and relations between the type of interactions and molecular disorder in the solid-state form of the compounds, have been explained.

INTRODUCTION

Owing to significant differences in physical and chemical properties between fluorine compounds and their hydrogen analogues, haloperfluorocarbons find wide applications in technology, agriculture, medicine and in other fields. The pharmacological activity of two enantiomers of a racemic halothane, widely used as a highly volatile general anaesthetic, is ascribed to their relative selective interactions with specific protein binding sites. In haloperfluorocarbons $[X(CF_2)_nX; X = Br \text{ or } I]$, the bromine or iodine atoms acquire a partial positive charge and they favourably form short interactions with electron rich nitrogen or oxygen containing Lewis bases. The halogen...halogen interactions can considerably change properties of substances; for example they may lead to solidification of fuels or other highly energetical compounds at ambient conditions. We also investigated pentafluoropyridine, where fluorine atoms are prone to nucleophilic substitution. The fluorinated-pyridine derivatives are used as liquid crystals, herbicides and antibiotics. This study on pressure-frozen pentafluoropyridine was aimed at investigating the preferences of the nitrogen and fluorine

atoms to form intermolecular contacts and molecular π -stacking association in the pure substance. Another fluorinated compound investigated was trifluoromethyl(trimethyl)silane. Silanes are important chemical compounds, owing to their physical and chemical properties. They are widely applied, for example in dentistry, medicine, construction technologies, synthesis, as adhesion promoters, coupling, crosslinking or dispersing agents and surface modifiers. Trimethyl(trifluoromethyl)silane, first synthesized in 1984 by Ingo Ruppert and commonly known as Ruppert's reagent, is used for syntheses of perfluorinated compounds and for introducing of a trifluoromethyl group by nucleophilic reaction. For these reasons the structural information about $(\text{CH}_3)_3\text{SiCF}_3$ are of particular interests. However to our knowledge, no crystal-diffraction results on $(\text{CH}_3)_3\text{SiCF}_3$ have been reported so far. Thus the aim of this study was to provide the structural information about this compound, and also to investigate the influence of the fluorine atoms and the molecule polarization for the intermolecular interactions and crystal packing.

The application of pressure in this study was aimed at revealing the compressibility of intermolecular contacts of halogen atoms, identifying the interactions governing the molecular association, eliminating the molecular disorder and determining the thermodynamical conditions favoring the cocrystallization of halogen...oxygen complexes. Pressure is an important thermodynamical parameter that has been often neglected in the studies of materials. Meanwhile pressure can considerably modify properties of substances and therefore should be taken into account in all processes where pressure change, e.g. for the ignition of fuels or triggered explosions. It was hoped, that by applying high-pressure techniques new phases of these compounds could be obtained, which would be considerably different from those frozen by cooling, and in this way new structure-properties would be revealed.

EXPERIMENTAL

Methodology

Structural x-ray diffraction studies were carried out on a 4-circle diffractometer KUMA KM-4 CCD, equipped with a CCD area detector (Figure 1). Diamond anvil cells of the Merrill-Bassett¹ type were designed and made in the Departmental workshop. Pressure in the DAC was calibrated by ruby-fluorescence method^{2,3}, using a Betsa PRL spectrometer, with an accuracy of 0.05 GPa. The CrysAlis version 1.171.24 software⁴ was used for the data collections⁵ and the preliminary reduction of the data. After the intensities were corrected for the effects of DAC absorption, sample shadowing by the gasket, and the sample absorption^{6,7}, the diamond reflections have been eliminated. All structures were solved straightforwardly by

direct methods⁸, and refined by full-matrix least-squares⁹. Anisotropic temperature factors were generally applied, but where the anisotropic refinement resulted in non-positive definite ellipsoids, isotropic thermal parameters were retained.

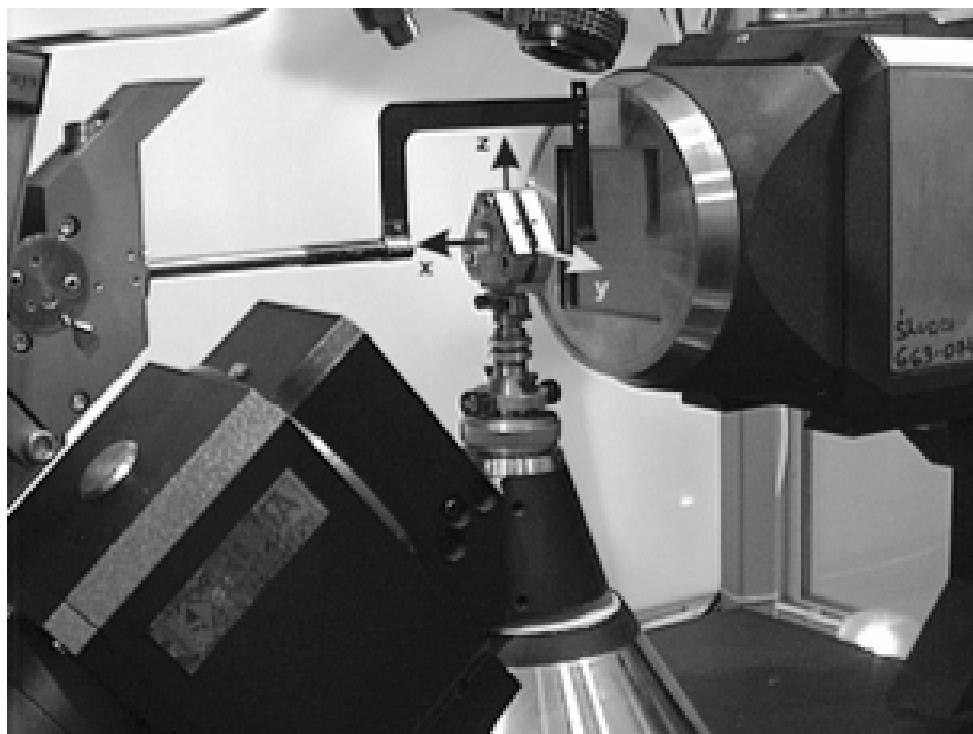


Figure 1. A diamond-anvil cell mounted on the KUMA KM-4 CCD diffractometer in the Faculty of Chemistry, Adam Mickiewicz University in Poznań.

Pressure freezing and X-ray determinations

1,2-diiodo-, 1,2-dibromo-, 1-bromo-2-iodoperfluoroethanes, pentafluoropyridine, 1-bromo-2-iodoperfluoroethane and 1,4-dioxane and trimethyl(trifluoromethyl)silane all have been in-situ pressure frozen in a Merrill-Bassett miniature diamond anvil cell (DAC)¹. The freezing pressure of particular compounds and mixture has been determined when the polycrystalline sample was in equilibrium with the liquid. The 1,2-diiodoperfluoroethane and 1,4-dioxane solidify when mixed at room temperature. The 1:1 cocrystal was melted by heating it to and in the liquid form loaded to a DAC. Single-crystal of each compound or mixture was obtained by heating polycrystalline mass in the DAC, till one seed was left, which was then grown by slowly lowering its temperature. The process of growing single-crystals of the substances investigated has been illustrated by the photographs in Figures 2-10.

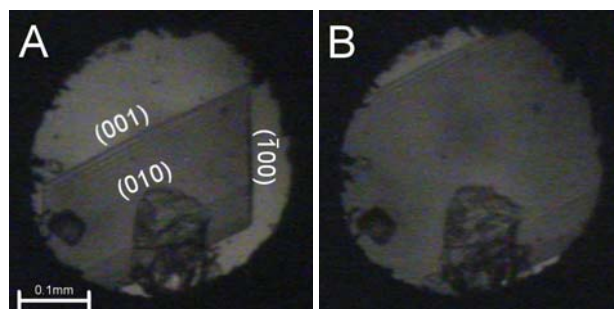


Figure 2. Two stages of the single-crystal growth of 1,2-dibromotetrafluoroethane: the plate-like crystal at 450 K (A), and the single-crystal covering almost all surface of the culet in the chamber at 330 K (B). Newton fringes can be observed for the very thin plate in photograph (A). Two ruby chips were placed in the chamber: the bigger one at the bottom of the photograph and the smaller to its left.

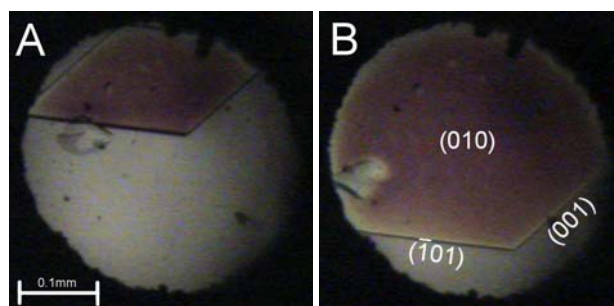


Figure 3. The pressure-frozen single crystal of 1,2-diiodoperfluoroethane in the DAC chamber at 443 K (A) and 383 K (B).

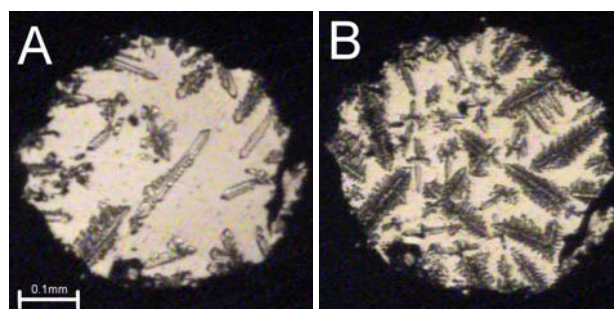
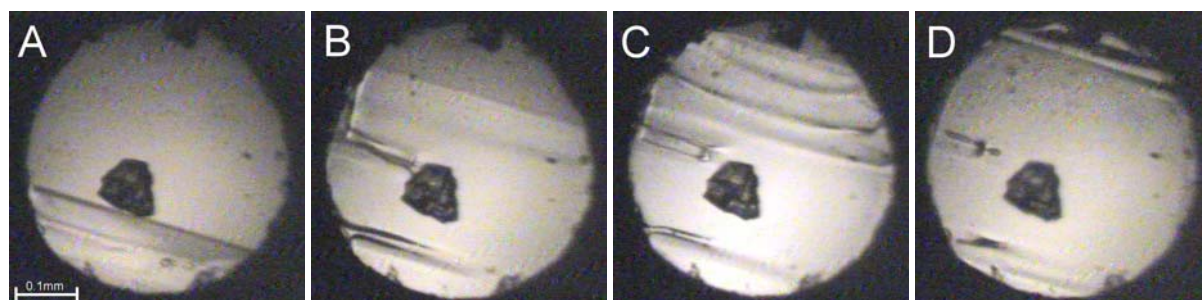


Figure 4. The pressure-frozen single crystal of 1,2-diiodoperfluoroethane at 453 K (A); and at 296 K/0.86 GPa (B) with small dendritic forms developed on the upper crystal face.



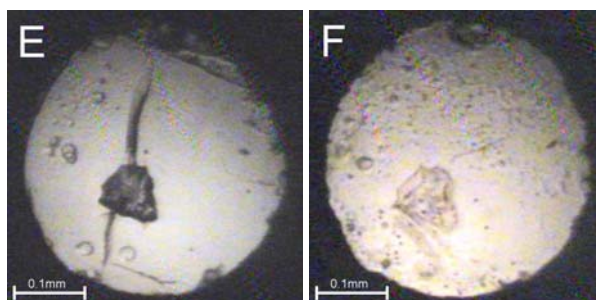


Figure 5. 1-Bromo-2-iodotetrafluoroethane single-crystal pressure freezing in the DAC chamber: 443 K (A); 393 K (B); 373 K (C); and at 296 K/0.6 GPa (D). Analogously obtained single crystals at 1.1 GPa (E) and 3.5 GPa (F) at room temperature. Two ruby chips for pressure calibration are placed one below the chamber center and other at its upper edge.

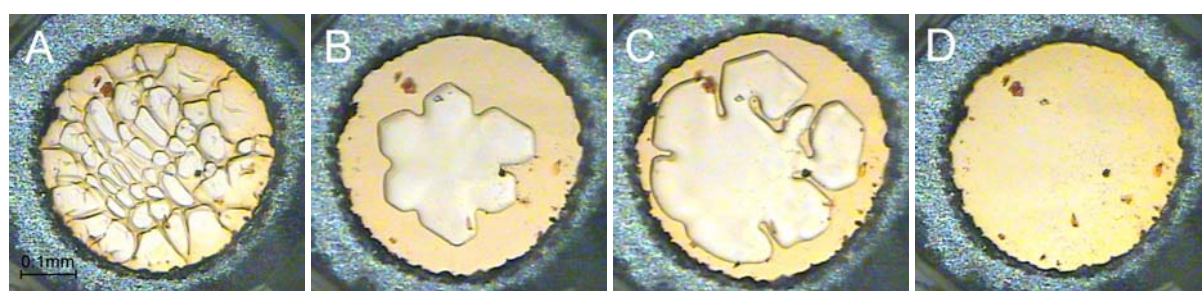


Figure 6. Isochoric growth of the 1,2-diiodoperfluoroethane:1,4-dioxane 1:1 cocrystal: (a) the melting process of the polycrystal sample at 400 K; (b) one single-crystal at 433 K and (c) at 395 K; (d) the single-crystal filling the whole volume of the DAC chamber at 296 K. Three small ruby chips for pressure calibration are located at the upper-left corner of the chamber. The yellow tint of the liquid is caused by impurities in the mixture, which condensed at high pressure and grouped between the cocrystal upper face (001) and the upper culet.

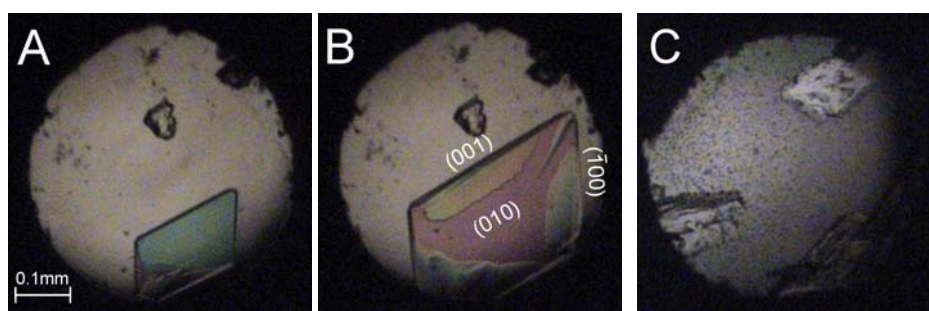


Figure 7. Isochoric growth stages of BrCF₂CF₂I:C₄H₈O₂ cocrystal: (A) a single-crystal seed at 393 K, (B) at 363 K with crystal faces indexed and (C) the cocrystal filling almost the whole volume of the DAC chamber at 296 K and 0.62 GPa, except for a few small additional crystals—for example the small grain in the upper right edge of the chamber is a twin small of the big crystal according to the mirror plane perpendicular to [100]. The ruby chip for pressure calibration, initially above the chamber center (A–B), has been pushed by the cocrystal to the chamber wall (C).

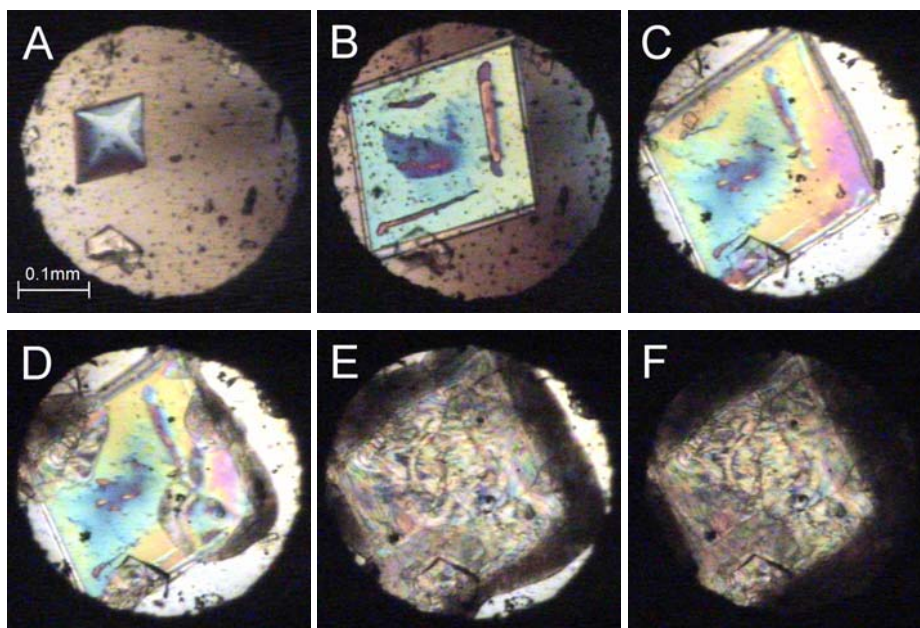


Figure 8. Separation of 1,4-dioxane from 1,2-dibromoperfluoroethane:1,4-dioxane mixture by pressure-freezing. (A) One 1,4-dioxane crystal grain left in the DAC chamber at 503 K; (B) this crystal at 483 K with clearly visible faults on its surfaces; (C) the self-repair process of the crystal at 473 K; (D) polycrystalline 1,2-dibromoperfluoroethane appearing at the upper left edge of the chamber at 443 K; and (E, F) the single-crystal of 1,4-dioxane and the polycrystals of 1,2-dibromoperfluoroethane filling the whole volume of the DAC. The ruby chip for pressure calibration is clearly seen above the bottom left edge of the chamber (A).

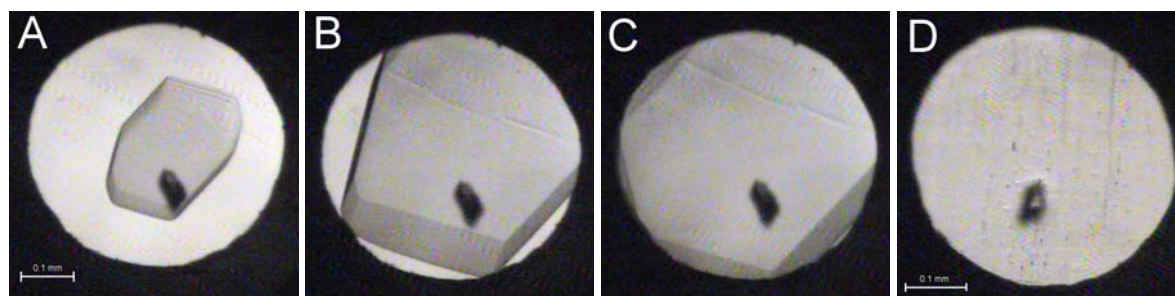


Figure 9. The growth stages of a single-crystal of perfluoropyridine at 1.1 GPa: (A) a single crystal seed at 433 K; (B) at 413 K; (C) at 403 K; and (D) the final form of the crystal at 1.1 GPa and 296 K. Newton fringes are visible on the upper edge of the seed in photograph (A). The vertical cracks in the crystal in photograph (D) are due to strains of the anisotropic sample cooled in the rigid chamber. The ruby chip for pressure calibration is visible below the chamber center.

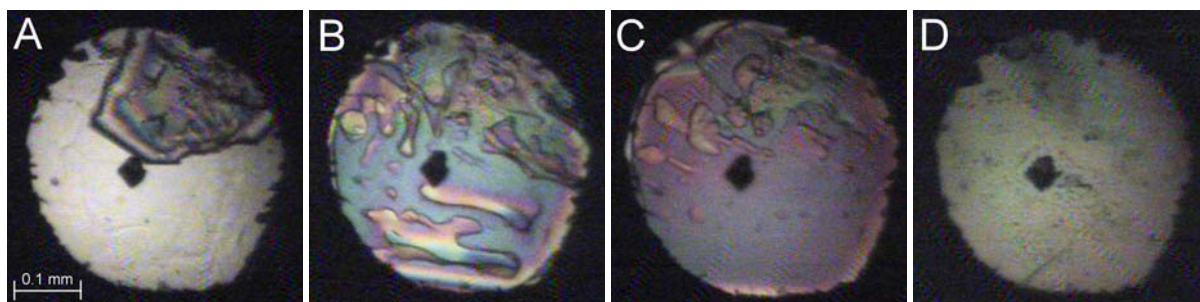


Figure 10. Isochoric-growth stages of the $(\text{CH}_3)_3\text{SiCF}_3$ single crystal: (A) distorted morphology of a small single crystal at 453 K; (B) the crystal at 333 K with its faces highly irregular; (C) the same crystal after 1 hour at 333 K; and (D) the crystal at room temperature and 0.9 GPa. The small ruby chip for pressure calibration is placed close to the centre of the DAC.

RESULTS

Disorder modes in isostructural dihaloperfluoroethanes

A group of isostructural crystals has been identified for a series of 1,2-dihalotetrafluoroethanes $\text{X}(\text{CF}_2)_2\text{Y}$ ($\text{X} = \text{Br}, \text{I}; \text{Y} = \text{Br}, \text{I}$). 1,2-Dibromotetrafluoroethane ($\text{BrCF}_2\text{CF}_2\text{Br}$), 1,2-diiodotetrafluoroethane ($\text{ICF}_2\text{CF}_2\text{I}$) and 1-bromo-2-iodotetrafluoroethane ($\text{BrCF}_2\text{CF}_2\text{I}$), have been in-situ pressure frozen in a diamond-anvil cell and their structures determined by X-ray diffraction. All the crystals are monoclinic, space group $P2_1/n$, with the midpoint of the C–C bond located at the centre of inversion (Figure 11). The freezing pressures of these compounds have been determined to be 0.80(5) GPa, 0.30(5) GPa and 0.10(5) GPa for $\text{BrCF}_2\text{CF}_2\text{Br}$, $\text{BrCF}_2\text{CF}_2\text{I}$ and $\text{ICF}_2\text{CF}_2\text{I}$, respectively.

In the structure of $\text{ICF}_2\text{CF}_2\text{I}$, the $-\text{CF}_2-\text{CF}_2-$ moiety is orientationally disordered about the intramolecular $\text{I}\cdots\text{I}$ axis at 0.16(5) GPa, but it becomes ordered at 0.86(5) GPa. The $\text{BrCF}_2\text{CF}_2\text{I}$ crystal structure is disordered in a different way: the $-\text{CF}_2-\text{CF}_2-$ is ordered but the Br and I atoms are substitutionally disordered with equal occupancies. The $\text{BrCF}_2\text{CF}_2\text{Br}$ structure is completely ordered. The formation of isostructural crystals by these compounds and different types of molecular disorder can be rationalized by the intermolecular interactions at varied thermodynamical conditions. The cohesion forces in these structures are dominated by $\text{I}\cdots\text{I}$, $\text{Br}\cdots\text{Br}$ and $(\text{Br/I})\cdots(\text{Br/I})$ contacts, but $(\text{Br/I})\cdots\text{F}$ contacts are considerably shorter in $\text{BrCF}_2\text{CF}_2\text{I}$ than in $\text{ICF}_2\text{CF}_2\text{I}$ and $\text{BrCF}_2\text{CF}_2\text{Br}$, which explains the absence of the $-\text{CF}_2-\text{CF}_2-$ disorder in this structure.

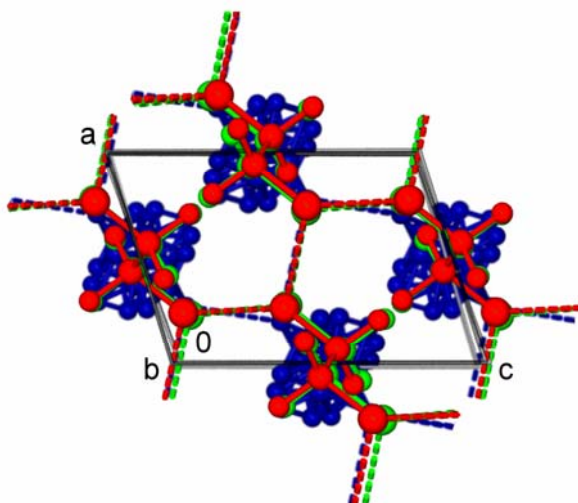


Figure 11. $\text{ICF}_2\text{CF}_2\text{I}$ (blue), $\text{BrCF}_2\text{CF}_2\text{I}$ (green) and $\text{BrCF}_2\text{CF}_2\text{Br}$ (red) unit cells and structures projected along $[010]$ and superimposed. The unit-cell dimensions of $\text{ICF}_2\text{CF}_2\text{I}$ have been adjusted to possibly precisely overlay unit-cell edges. The applied scaling factors for a and c were: 0.88:1.00, respectively.

Halogen \cdots oxygen interactions and disorder modes in pressure frozen complexes of 1,2-dihalo-perfluoroethanes with 1,4-dioxane

1,2-Diiodo-, 1,2-dibromo- and 1-bromo-2-iodoperfluoroethanes in 1:1 mixtures with 1,4-dioxane were pressure frozen in a diamond-anvil cell. Structures of cocrystal of 1,2-diiodoperfluoroethane:1,4-dioxane at 0.30(5) GPa/296(2) K and of 1-bromo-2-iodoperfluoroethane:1,4-dioxane at 0.62(5) GPa/296 K were determined by single-crystal X-ray diffraction. Also the single-crystal of 1,4-dioxane separated from 1,2-dibromoperfluoroethane, which reminded liquid, was investigated at 0.42 GPa/296 K. The cocrystal of $\text{ICF}_2\text{CF}_2\text{I}:\text{C}_4\text{H}_8\text{O}_2$ and the 1,4-dioxane crystal are isostructural with their phases frozen by cooling; the $\text{BrCF}_2\text{CF}_2\text{I}:\text{C}_4\text{H}_8\text{O}_2$ cocrystal has not been reported earlier. In the structure of $\text{ICF}_2\text{CF}_2\text{I}:\text{C}_4\text{H}_8\text{O}_2$ the $-\text{CF}_2-\text{CF}_2-$ moiety is disordered about the $\text{I}\cdots\text{I}$ molecular axis and $\text{C}_4\text{H}_8\text{O}_2$ molecule rotate about the $\text{O}\cdots\text{O}$ molecular axis too; and in $\text{BrCF}_2\text{CF}_2\text{I}:\text{C}_4\text{H}_8\text{O}_2$ the Br and I atoms are disordered in this way that they possess the same position with half occupancy, but the molecule of $\text{C}_4\text{H}_8\text{O}_2$ is ordered in this complex, and it is also ordered in the structure of the single crystal obtained from the $\text{BrCF}_2\text{CF}_2\text{Br}:\text{C}_4\text{H}_8\text{O}_2$ mixture.

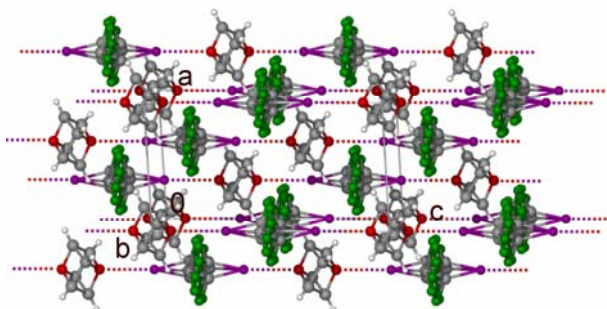


Figure 12. The molecular packing of 1,2-diiodoperfluoroethane:1,4-dioxane cocrystal at 0.30GPa/296K. The shortest I \cdots O contacts have been indicated as dashed lines, and the disordered sites of the -CF₂-CF₂- and -CH₂-CH₂- moieties have been shown.

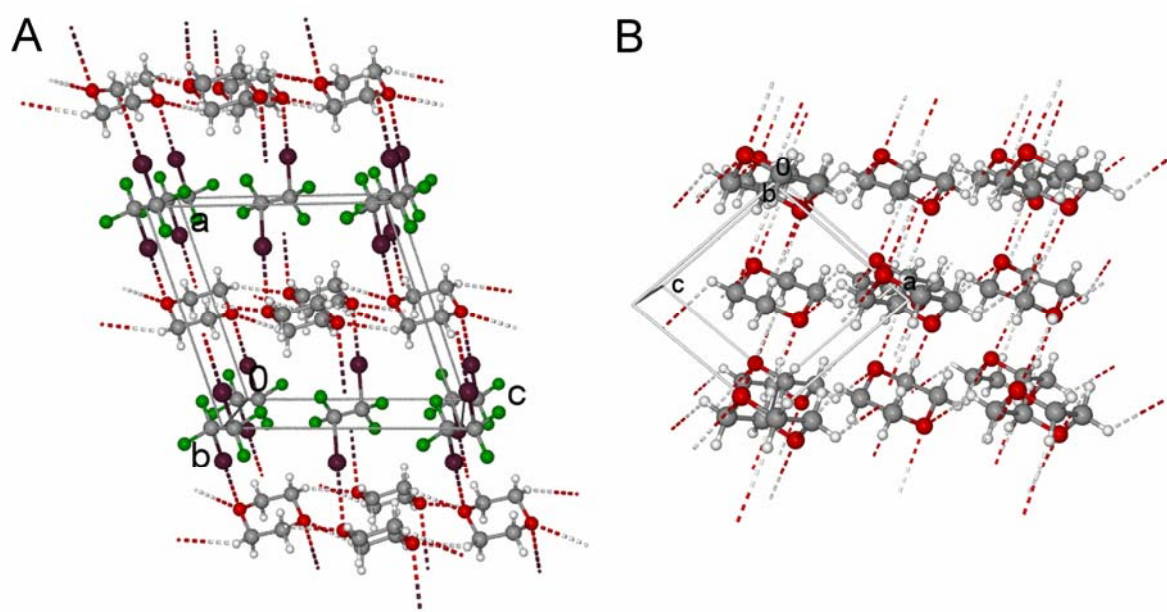


Figure 13. The molecular packing of (A) 1,2-dibromoperfluoro:1,4-dioxane cocrystal with the shortest Br/I \cdots O interactions of 2.93(2) Å and O \cdots H of 2.592 Å at 0.62 GPa/296 K; and (B) 1,4-dioxane with two shortest O \cdots H contacts of 2.655 Å and 2.672 Å at 0.42 GPa/296 K.

Intermolecular interactions in pressure frozen pentafluoropyridine crystal, its structure and compressibility at 0.3 and 1.1 GPa

Pentafluoropyridine, C₅F₅N, has been in-situ pressure frozen in a diamond-anvil cell (DAC) and its structure determined at 0.30(5) GPa and 1.10(5) GPa and at room temperature by single-crystal X-ray diffraction. The freezing pressure of pentafluoropyridine has been determined to be 0.10(5) GPa. The crystals are monoclinic, space group *P2*₁/*c*. The crystal packing is governed by F \cdots F and C/N \cdots F van der Waals contacts, but no ring stacking is

observed. The geometry of contacts suggests that the intermolecular interactions are non-directional, and the crystal compresses nearly isotropically between 0.3 and 1.1 GPa.

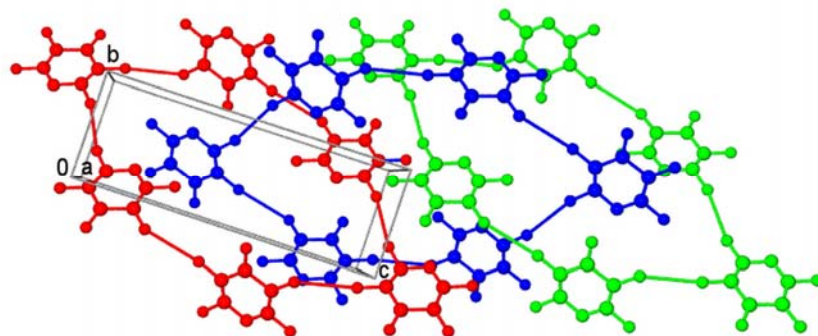


Figure 14. The interpenetrating hexamers (in different colours for clarity) of molecules forming F...F contacts.

Pressure freezing and crystal structure of trimethyl(trifluoromethyl)silane

Trimethyl(trifluoromethyl)silane, $(\text{CH}_3)_3\text{SiCF}_3$, has been in-situ pressure frozen in a diamond anvil cell and its structure determined at 0.9 GPa/296 K by single-crystal X-ray diffraction. Crystal is monoclinic, space group $P2_1/m$ with molecules lying on the crystallographic mirror plane and the CH_3 and CF_3 groups are in the fully staggered conformation. The 12-fold coordination of the molecules is similar to that in $(\text{CH}_3)_3\text{SiCl}$, but different from $(\text{CH}_3)_4\text{Si}$. The shortest intermolecular contacts in the structure of pressure-frozen $\text{CF}_3\text{Si}(\text{CH}_3)_3$ are observed between fluorine and hydrogen atoms.

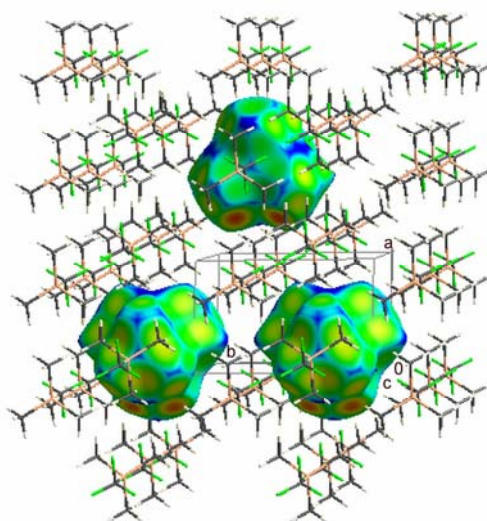


Figure 15. The intermolecular interactions represented by a colour scale on the Hirshfeld surface. The property mapped onto the surface is the distance from its element to the nearest exterior atom and it ranges from 1.00 Å (red) to 2.00 Å (blue) in this picture.

CONCLUSIONS

The high-pressure studies on 1,2-dihalo-perfluoroethanes and their complexes with 1,4-dioxane, 1:1 mol, revealed the molecular disorder, the patterns of intermolecular interactions and the ability of I and Br/I atoms to form short contacts with oxygen. However, the $\text{Br}\cdots\text{O}$ contacts have not been observed as pure $\text{BrCF}_2\text{CF}_2\text{Br}$ does not cocrystallize with $\text{C}_4\text{H}_8\text{O}_2$. The pressure freezing of $\text{BrCF}_2\text{CF}_2\text{Br}:\text{C}_4\text{H}_8\text{O}_2$, 1:1 mixture, resulted in a single crystal of $\text{C}_4\text{H}_8\text{O}_2$. At these conditions $\text{BrCF}_2\text{CF}_2\text{Br}$ remains liquid. The formation of the $\text{BrCF}_2\text{CF}_2\text{Br}:\text{C}_4\text{H}_8\text{O}_2$ cocrystal could be additionally hampered by the big difference in melting points of 161.65 K for $\text{BrCF}_2\text{CF}_2\text{Br}$ and 285 K for $\text{C}_4\text{H}_8\text{O}_2$. It has been shown also for $\text{ICF}_2\text{CF}_2\text{I}$, that the disorder of $-\text{CF}_2-\text{CF}_2-$ moieties can be eliminated by increasing pressure.

The crystal structure of perfluoropyridine revealed only weak intermolecular interactions and contacts commensurate with the sums of atomic van der Waals radii. The isotropic compression of $\text{F}\cdots\text{F}$ and $\text{N}\cdots\text{F}$ contacts suggests that directional forces markedly stronger than others are formed to 1.1 GPa.

The study on the crystal structure of trimethyl(trifluoromethyl)silane confirmed that the $\text{Si}-\text{CF}_3$ bond is longer and weaker than the $\text{Si}-\text{CH}_3$ bonds. It has been confirmed that there are no strong intermolecular interactions in $(\text{CH}_3)_3\text{SiCF}_3$ and that its structure is isostructural with $(\text{CH}_3)_3\text{SiCl}$ in phase α and the molecular coordination scheme is similar to those in $(\text{CH}_3)_3\text{SiCl}$ both phases α and β , but very different from that in $(\text{CH}_3)_4\text{Si}$. However, the absence of strong intermolecular interactions is the common feature of all these silanes investigated.

The studies performed showed that the pressure crystallization is very convenient for obtaining single crystals of molecular substances, even when it was very difficult to obtain these crystals by other methods. For example, a phenomenon of self-repairing the crystals in the DAC was observed – we termed it as self-healing effect.

The results of the studies have been presented at several conferences, both in the US and in Poland, and also prepared in the form of scientific articles currently being submitted for publication:

- 1) "Intermolecular interactions in pressure frozen pentafluoropyridine crystal, its structure and compressibility at 0.3 and 1.1 GPa"; Olejniczak, A., Katrusiak, A. and Vij, A.; submitted for security clearance in August, 2006, for publication in Journal of Fluorine Chemistry;

- 2) "Disorder modes in isostructural dihaloperfluoroethanes"; Olejniczak, A., Katrusiak, A. and Vij, A.; submitted for security clearance in November, 2006, for publication in *Crystal Growth&Design*;
- 3) "Halogen···oxygen interactions and disorder modes in pressure frozen complexes of 1,2-dihaloperfluoroethanes with 1,4-dioxane"; Olejniczak, A., Katrusiak, A. and Vij, A.; submitted for security clearance in February, 2007, for publication in *Crystal Growth & Design*;
- 4) "Pressure freezing and crystal structure of trimethyl(trifluoromethyl)silane"; Olejniczak, A., Katrusiak, A. and Vij, A.; prepared April 2007 for publication in *Acta Crystallographica Section B*.

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